33. CHEMICAL EVIDENCE FOR NEAR-SEAFLOOR PRECIPITATION OF CALCITE IN SERPENTINITES (SITE 897) AND SERPENTINITE BRECCIAS (SITE 899), IBERIA ABYSSAL PLAIN¹

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ABSTRACT

Stable isotopic and trace-element analyses of vein-filling calcite in serpentinite at Site 897 and in serpentinite breccias at Site 899 suggest precipitation at low temperature (10° to <20°C) from seawater in the Early to middle Cretaceous. Trace amounts of Fe and Mn in the calcites are in excess of amounts expected from unmodified seawater and suggest mobilization of these elements from the serpentinites. Narrow variation of isotopic values (δ^{18} O, δ^{13} C, and 87 Sr/ 86 Sr) across texturally variable calcite types demonstrates that the isotopic composition of calcite-precipitating fluids was not strongly affected by rock dissolution or mineral precipitation. Given the degree of alteration observed in the noncarbonate fraction of these rocks, a high water/rock ratio during calcitization of the serpentinitic materials is implied. Mg and Sr concentrations in vein calcites at these sites are low (typically <4 mole% for Mg and below detection for Sr) in comparison to authigenic calcite in shallow-marine diagenetic settings.

INTRODUCTION

Calcitized serpentinites recovered at Ocean Drilling Program (ODP) Sites 897 and 899 provide a useful model for understanding the textural and chemical evolution of ophicarbonates. Textural and chemical attributes established early in the history of rifting can be examined in these formerly exposed mantle materials, without the subsequent tectonic overprinting that characterizes ophiolitic materials exposed in mountain belts (e.g., Weissert and Bernoulli, 1984; Früh-Green et al., 1990). The relatively simple postrifting burial history at Sites 897 and 899 (Shipboard Scientific Party, 1994a, 1994b) provides a relatively well-constrained context for interpretation of chemical data. A close analogy can be drawn between the calcitized serpentinites at Sites 897 and 899 and previously described carbonate-enriched ultramafic rocks at mid-ocean ridges (e.g., Bonatti et al., 1974, 1980) and seaward of the Galicia margin (Agrinier et al., 1988; Kimball and Evans, 1988). Samples recovered during Leg 149 span the sediment/basement contact and extend nearly 200 m into serpentinitic materials at both sites, allowing examination of ophicarbonate generation in unprecedented detail.

This study undertakes to evaluate the timing and conditions of precipitation of fracture-filling calcite in serpentinitic basement samples at Sites 897 and 899 using trace-element (Mg, Fe, Mn, and Sr) and isotopic (δ^{18} O, δ^{13} C, and 87 Sr/⁸⁶Sr) analyses. Petrographic evidence on the paragenesis of fracturing and calcite precipitation is presented in a companion paper by Morgan and Milliken (this volume); stratigraphic trends in calcite distribution and the effects of calcite precipitation on bulk composition are discussed in the *Initial Reports* site chapters (Shipboard Scientific Party, 1994a, 1994b) and by Gibson et al. (this volume) and Milliken et al. (this volume).

Constraints drawn from the above-cited works on the serpentinites of the Iberia Abyssal Plain, together with the geochemical data

¹Whitmarsh, R.B., Sawyer, D.S., Klaus, A., and Masson, D.G. (Eds.), 1996. *Proc. ODP*, *Sci. Results*, 149: College Station, TX (Ocean Drilling Program).

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presented here, strongly suggest that the vein-filling calcite at both sites was precipitated at 10° to <20°C from a fluid that was isotopically similar to Early to middle Cretaceous seawater. Mg and Sr contents are unusually low for marine precipitates and may reflect the rather low temperatures of precipitation. Trace amounts of Fe and Mn in the calcite were mobilized from the serpentinites through dissolution. Several lines of evidence suggest calcite precipitation in a system characterized by very high water/rock ratios.

SAMPLING AND ANALYSIS METHODS Samples

Samples utilized in this study are a subset of samples used for petrographic (standard light microscopy and cathodoluminescence) study of calcite veins (Morgan and Milliken, this volume). Trace-element analysis was performed on the same thin sections used for petrographic study. Backscattered electron imaging was routinely employed for sample navigation in the electron microprobe. Powders for isotopic analyses were obtained from rock slabs taken adjacent to the thin-section blanks. Powders were excavated with a micro-drill bit (approximately 0.5 mm diameter) from specific calcite types identified on the basis of their petrographic characteristics. This method allows only a relatively crude discrimination of the myriad complex zones within the calcites. All isotopic values necessarily represent mixtures of calcite types, construed to be dominated by some specific type that was the target of microdrilling.

Trace-element Analysis

Wavelength-dispersive analysis of trace elements was performed on a JEOL 733 electron microprobe at the University of Texas at Austin. Cathodoluminescence and plane-polarized light images of vein calcites (Morgan and Milliken, this volume) were used as a guide to beam placement. Analysis was performed with a 15-kV accelerating voltage, a sample current of 12 nA (measured on brass), and a 10-µm spot. Calibrations were performed using standard carbonate materials: dolomite (for Ca, Mg), siderite (for Fe, Mn), and coral (for Sr) that are part of the standard collection in the University of Texas Electron Microprobe Laboratory. Analysis times employed were 60 s for Sr and 20 s for all other elements. Totals between 97 and 103 were accepted. Detection limits were approximately 340 ppm for Mg, 450 ppm for Fe, 310 ppm for Mn, and 185 ppm for Sr.

Carbon and Oxygen Isotopic Analysis

Powders obtained by microdrilling were reacted under vacuum with 100% phosphoric acid at 25°C (method of McCrea, 1950) and analyzed on a VG Prism gas-source mass spectrometer (University of Texas at Austin).

Strontium Isotopic Analysis

Powders obtained by microdrilling were analyzed on a Finnigan-Mat 261 thermal ionization mass spectrometer. For comparison to values for seawater Sr on the Burke curve (Burke et al., 1982; Koepnick et al., 1985) it is necessary to subtract 0.0001 from the values reported here (L.M. Mack, pers. comm., 1994).

RESULTS

Trace Elements

Most of the vein calcites at both sites are relatively pure $CaCO_3$ (Table 1). Calcite at Site 897 averages 97.5 mole% $CaCO_3$ (64 analyses), ranging from 93 to >99 mole%; calcite at Site 899 averages 98.5 mole% $CaCO_3$ (295 analyses), ranging from 96 to >99 mole%. No strong covariation of trace-element concentrations is apparent in the data set as a whole (Fig. 1).

Many of the vein calcites contain Fe and Mn considerably in excess of concentrations expected for precipitation from unmodified seawater (cf., Veizer, 1983, p. 269). Concentrations of Fe and Mn are relatively low, however, in comparison to values observed in authigenic calcites in many sedimentary basins (K.L. Milliken, unpubl. data). The very low Mg and Sr (average below detection in four samples) concentrations are also atypical of authigenic calcite in shallow-marine settings, though they approach values believed consistent with precipitation from cold seawater (Morse and Mackenzie, 1990, pp. 93-101).

Within individual samples, variations in trace-element concentrations are also rather unsystematic across both the petrographic types of calcites and the temporal sequences of calcite types identified by Morgan and Milliken (this volume). Figure 2 and Table 2 present data for Sample 149-899B-16R-2, 69-72 cm, as an example. In this sample, at least three petrographically distinct generations of calcite were observed: an early generation of highly vacuolized calcite with a radial fabric (botryoidal); a subsequent generation of brightly luminescent clear sparry calcite that fills the central portion of the large veins and also small cracks localized between the vacuolized calcite and the serpentinite; and, finally, a late generation of calcite with dark luminescence that fills small fractures that crosscut the earlier generations (Morgan and Milliken, this volume). As expected (e.g., Hemming et al., 1989; Machel et al., 1991), the dark luminescence corresponds either to marginally higher Fe concentrations or to very low amounts of both Fe and Mn, and bright luminescence occurs in zones with overall higher Mn concentrations. However, the petrographically distinct calcite types do not have mutually exclusive fields of traceelement concentrations for any of the elements analyzed nor are there consistent trends for any element across the temporal sequence of calcite types.

Comparison of petrographic types of calcite across different samples also reveals unsystematic variation. For example, a crossplot of Mg content vs. Mn content for botryoidal calcite in two samples, one from Site 897 and the other from Site 899, reveals that petrographic similarity does not correspond to similarity in trace elements (Fig. 3), which is consistent with the observed difference in luminescence between these different samples of vacuolized calcite. In terms of Mg and Mn concentrations, vacuolized calcite in the Site 899 sample is more similar to some of the nonvacuolized calcite in the same sample than it is to vacuolized calcite in the sample from Site 897.

Surviving aragonite was identified in only Sample 149-897D-16R-4, 0-5 cm, on the basis of distinctive petrographic characteristics (confirmed by X-ray diffraction; Morgan and Milliken, this volume). Analysis of the aragonite reveals very high Sr contents and little substitution by other trace elements (Table 3).

Carbon and Oxygen Isotopes

Carbon and oxygen isotopic compositions of vein calcites (Table 4, Fig. 4) display a total range of 1.76‰ for δ^{18} O and 3.4‰ for δ^{13} C. As with trace-element variation, there is no systematic variation of δ^{18} O and δ^{13} C among petrographically distinct calcite types. Average isotopic compositions do not vary significantly between Site 897 and Site 899 and are very similar to isotopic values observed for carbonates in serpentinites drilled at Hole 637A during ODP Leg 103, in the region seaward of Galicia Bank (Evans and Baltuck, 1988).

Sr Isotopes

Eleven samples manifest a narrow range for ⁸⁷Sr/⁸⁶Sr (from 0.70735 to 0.70754, Table 4), a range that is, nevertheless, in excess of analytical error. ⁸⁷Sr/⁸⁶Sr does not vary in any systematic way with petrographic types of calcite. Associated vacuolized and clear calcites were analyzed in three samples. Variation in ⁸⁷Sr/⁸⁶Sr between vacuolized calcites and associated clear calcites is less than the variation among vacuolized calcites in the data set as a whole.

DISCUSSION

Timing of Calcite Precipitation

At Site 897, calcite was precipitated within the serpentinites prior to their incorporation in the mass flow unit of late Hauterivian to late Aptian age (Shipboard Scientific Party, 1994a), whereas at Site 899, fracturing and calcitization postdate deposition of the serpentinite breccia and the underlying mass flow unit of Barremian to Aptian age (Shipboard Scientific Party, 1994b; Gibson et al., this volume).

Comparison with the Sr isotopic curve for Cretaceous seawater (Jones et al., 1994) reveals that ⁸⁷Sr/⁸⁶Sr values at both sites are consistent with the timing inferred from stratigraphy (Fig. 5). Early to middle Jurassic times for alteration fall within the observed range of ⁸⁷Sr/⁸⁶Sr in the calcite, but are deemed implausible because such ages predate the time of rifting. The earliest possible time for pre-massflow calcitization at Site 897, as determined from the observed ⁸⁷Sr/ ⁸⁶Sr, is somewhat older than the inferred time of rifting (approximately 130 Ma; Sawyer, Whitmarsh, Klaus, et al., 1994); calcitization essentially concomitant with deposition of the mass-flow unit is also possible. The youngest possible age of the post-mass-flow calcite precipitation at Site 899 (determined from the highest observed ⁸⁷Sr/ ³⁶Sr value of 0.70754) can be constrained only as older than Campanian. Younger ages for calcitization are not possible because the ^{8/}Sr/ ⁸⁶Sr of seawater did not fall below 0.7076 in the post-Cretaceous. This is consistent with biostratigraphic data that constrain the sediment immediately overlying the altered zone at the top of the breccia to a Campanian-Maastrichtian age (Shipboard Scientific Party, 1994b). Further analysis of stratigraphic variation of ⁸⁷Sr/⁸⁶Sr in calcite and other authigenic phases (e.g., clays) at Sites 897 and 899 may provide more details about the timing and sequences of basement alteration.

Constraints on Temperature and Fluid Composition

Fe and Mn in the calcites are plausibly interpreted to have been mobilized into the pore fluid during dissolution of silicate components in the serpentinites. Derivation of these elements from the over-

Table 1. Electron microprobe analyses of elements in fracture-filling calcites, averaged for Sites 897 and 899.

| | CaCO ₃ (mole%) | MgCO ₃ (mole%) | FeCO ₃ (mole%) | MnCO ₃ (mole%) | SrCO ₃ (mole%) | Mg (ppm) | Fe (ppm) | Mn (ppm) | Sr (ppm) |
|------------------|------------------------------|------------------------------|------------------------------|------------------------------|------------------------------|-------------|-------------|-------------|-------------|
| Site 897 | | | | | | | | | |
| Number | 64 | 64 | 64 | 64 | 24 | 64 | 24 | 64 | 64 |
| Average | 97.47 | 2.13 | 0.20 | 0.20 | 0.02 | 5146 | 1112 | 1067 | 177 |
| Minimum | 93.12 | BDL | BDL. | BDL. | BDL | BDL | BDL | BDL | BDL |
| Maximun | 99.85 | 6.20 | 0.95 | 1.04 | 0.05 | 14850 | 5157 | 5702 | 470 |
| Site 899 | | | | | | | | | |
| Number | 295 | 295 | 295 | 295 | 28 | 295 | 295 | 295 | 28 |
| Average | 98.54 | 1.29 | 0.04 | 0.12 | 0.00 | 3153 | 244 | 688 | 12 |
| Minimum | 96.04 | BDL | BDL. | BDL. | BDL | BDL | BDL | BDL | BDL |
| Maximun | 99.98 | 3 73 | 0.80 | 1.47 | 0.02 | 9250 | 4394 | 8027 | 170 |
| 1. Id., tittlett | ,,,,,, | 0.10 | 0.00 | | 0.01 | 1000 | 1071 | 00107 | 110 |



Figure 1. Trace-element variations in fracture-filling calcites, Sites 897 and 899. A. Fe vs. Mg. B. Mn vs. Mg.



Figure 2. Mn vs. Mg variation among different types and generations of calcite in Sample 149-899B-16R-2, 69-72 cm. See text for further description of calcite types.

lying sediment column is precluded by the Sr isotopic evidence discussed above. Petrographic evidence for intermittent precipitation of Fe oxides in highly weathered serpentinite and serpentinite breccias (Milliken et al., this volume) suggests a plausible local sink for dissolved oxygen, which could have led to fluctuations in the oxidation state of the fluid and its dissolved Fe and Mn. However, the range and uniformity of isotopic values in calcite suggest that fluid/rock interactions did not cause a detectable shift in fluid composition away from normal marine values for δ^{13} C, δ^{18} O, and ⁸⁷Sr.⁸⁶Sr.

Figure 6 shows a range of temperature and $\delta^{18}O_{H_2}O$ that are consistent with the range of $\delta^{18}O_{calcite}$ observed. Precipitation of these calcites from unmodified seawater (0‰, standard mean ocean water [SMOW]) requires temperatures in the range of 10° to 17°C. The $\delta^{18}O_{calcite}$ values are about 2‰-3‰ lighter than those observed in cal-

cites associated with mid-ocean-ridge ophicarbonates (Bonatti et al., 1974). Values observed by Bonatti et al. are consistent with temperatures of precipitation very near 0°C.

Unfortunately, uncertainties in the geologic history of mantle exposure at Sites 897 and 899, especially with regard to the earliest stages of rifting, allow wide latitude for interpreting the conditions of calcite precipitation. Based on the tectonic setting alone, fluids ranging from -5 % to +7% can be postulated; temperatures ranging from near 0° to >100°C are possible.

Precipitation of calcite from strictly meteoric fluids can probably be ruled out on the basis of the apparent marine ⁸⁷Sr/⁸⁶Sr signature together with whole-rock rare-earth element (REE) patterns suggesting a strong marine diagenetic overprint (Milliken et al., this volume). However, fluids other than a O‰ seawater still can be postulated under several scenarios. Glacial cycles shift $\delta^{18}O_{seawater}$ by about $\pm 1\%$ (e.g., Arthur et al., 1983). Modification of fluids in submarine diagenetic environments can shift δ^{18} OH₂O into the range of negative values by several possible mechanisms. Precipitation of copious quantities of authigenic phases at very low temperatures (e.g., Lawrence and Gieskes, 1981), recharge of meteoric fluids into submarine aquifers (e.g., Manheim and Paull, 1981), and expulsion of unmodified, relict meteoric water from rocks buried in a marine environment (e.g., Gieskes et al., 1994) are examples of mechanisms for producing ¹⁸O-depleted pore fluids in marine settings. Interpreted excursions of δ^{18} OH₂O to values below about -3‰ at 0° to 5°C can be excluded for our data set because such values lead to the prediction of improbably low temperatures. Any ¹⁸O-depleted (negative) fluid at temperatures >17°C is inconsistent with observed $\delta^{18}O_{calcite}$, which again probably rules out any direct (i.e., surficial) meteoric exposure. A slightly ¹⁸O-depleted fluid in the temperature range of 5° to 17°C cannot be excluded as a possible agent of calcite precipitation. Expulsion of depleted fluids from underlying (or adjacent) basinal sediments seems unlikely for these basement rocks, especially given the volume of fluids necessary to account for the large amount of calcite that is

Table 2. Example of compositional variations among different petrographic types of calcite, Sample 149-899B-16R-2, 69-72 cm.

| Analysis | CaCO ₃ (mole%) | MgCO ₃ (mole%) | FeCO ₃ (mole%) | MnCO ₃ (mole%) | Mg (ppm) | Fe (ppm) | Mn (ppm) |
|------------|------------------------------|------------------------------|------------------------------|------------------------------|--------------|-------------|-------------|
| Early vacu | uolized calo | cite | | | | | |
| 1F | 98.89 | 0.99 | 0.05 | 0.06 | 2436 | 283 | 320 |
| 3C | 97.77 | 2.04 | 0.06 | 0.13 | 4914 | 320 | 693 |
| 3D | 98.91 | 1.02 | 0.03 | 0.03 | 2467 | 169 | 189 |
| 3E | 99.23 | 0.69 | 0.05 | 0.03 | 1673 | 251 | 175 |
| 30 | 98.98 | 1.02 | 0.00 | 0.00 | 2520 | 0 | 0. |
| 3P | 99.05 | 0.95 | 0.00 | 0.00 | 2416 | 0 | 0 |
| 3Q | 99.24 | 0.76 | 0.00 | 0.00 | 1861 | 0 | 0 |
| 30-1 | 99.21 | 0.79 | 0.00 | 0.00 | 2017 | 0 | 0 |
| 30-2 | 99.33 | 0.67 | 0.00 | 0.00 | 1649 | 0 | 20 |
| 30-3 | 99.50 | 0.49 | 0.00 | 0.01 | 1228 | 0 | 30 |
| 3U-4 | 99.37 | 0.63 | 0.00 | 0.00 | 1604 | 0 | 0 |
| Liear spar | Ty calcite 1 | n veins of if | | age | 1272 | 195 | 272 |
| IG | 99.39 | 1.02 | 0.05 | 0.07 | 2458 | 103 | 866 |
| 16 | 97.25 | 2.46 | 0.03 | 0.25 | 6098 | 157 | 1420 |
| 11 | 98.45 | 1 33 | 0.03 | 0.18 | 3272 | 170 | 000 |
| IP | 97.99 | 1.87 | 0.03 | 0.10 | 4550 | 216 | 564 |
| 10 | 98.03 | 1.85 | 0.02 | 0.09 | 4525 | 131 | 500 |
| ÎR | 99.28 | 0.58 | 0.08 | 0.06 | 1384 | 453 | 317 |
| 2B | 97.90 | 1.92 | 0.02 | 0.15 | 4647 | 113 | 824 |
| 2J | 98.22 | 1.49 | 0.03 | 0.27 | 3515 | 141 | 1423 |
| 2K | 97.17 | 2.49 | 0.06 | 0.28 | 5901 | 328 | 1503 |
| 3F | 98.56 | 1.31 | 0.06 | 0.06 | 3178 | 361 | 325 |
| 3H | 98.69 | 1.14 | 0.02 | 0.15 | 2743 | 86 | 816 |
| 31 | 98.62 | 1.14 | 0.11 | 0.12 | 2879 | 657 | 696 |
| 3M | 98.62 | 1.21 | 0.07 | 0.10 | 2982 | 372 | 552 |
| 3N | 98.55 | 1.23 | 0.06 | 0.16 | 3161 | 344 | 912 |
| 3R | 98.36 | 1.30 | 0.00 | 0.34 | 3233 | 0 | 1916 |
| 3S | 98.76 | 1.19 | 0.00 | 0.05 | 3069 | 0 | 285 |
| 3T 3V | 98.62 99.13 | $1.10 \\ 0.77$ | 0.00 | 0.27 | 2762 1918 | 0 | 1563 536 |
| Clear spar | TV calcite i | n late fractu | res | 0110 | 1910 | 0 | 000 |
| 10 | 98.96 | 0.86 | 0.18 | 0.00 | 2162 | 1041 | 0 |
| 1D | 99.32 | 0.60 | 0.05 | 0.03 | 1482 | 239 | Ő |
| 1H | 99.19 | 0.63 | 0.15 | 0.03 | 1508 | 818 | 169 |
| 1J | 99.30 | 0.50 | 0.07 | 0.12 | 1231 | 424 | 686 |
| 1M | 99.43 | 0.47 | 0.09 | 0.00 | 1127 | 510 | 0 |
| 1N | 99.21 | 0.67 | 0.11 | 0.00 | 1618 | 623 | 0 |
| 10 | 99.33 | 0.63 | 0.02 | 0.01 | 1556 | 88 | 71 |
| 10' | 98.87 | 0.98 | 0.15 | 0.00 | 2376 | 822 | 0 |
| 1T | 99.51 | 0.34 | 0.12 | 0.02 | 804 | 635 | 129 |
| 2A | 98.31 | 0.88 | 0.80 | 0.00 | 2111 | 4394 | 0 |
| 2A' | 99.34 | 0.62 | 0.02 | 0.01 | 1495 | 99 | 53 |
| 2D 2E | 98.15 | 1.74 | 0.09 | 0.01 | 4290 | 538 | 44 |
| 2E 2E' | 98.30 | 1.70 | 0.00 | 0.00 | 4100 | 0 | 16 |
| 26 | 99.70 | 0.92 | 0.00 | 0.00 | 2207 | 14 | 10 |
| 26 | 99.00 | 1.04 | 0.00 | 0.00 | 2527 | 194 | 60 |
| 20 | 08.65 | 1.04 | 0.03 | 0.01 | 3110 | 127 | 00 |
| 2H | 99.09 | 0.86 | 0.02 | 0.00 | 2101 | 310 | ő |
| 21 | 98.86 | 1.13 | 0.00 | 0.00 | 2741 | 0 | ő |
| 2L | 99.16 | 0.75 | 0.09 | 0.00 | 1804 | 484 | ŏ |
| 2M | 98.99 | 0.87 | 0.11 | 0.02 | 2101 | 598 | 129 |
| 3A | 98.64 | 1.17 | 0.18 | 0.01 | 2739 | 953 | 70 |
| 3B | 97.17 | 1.64 | 0.15 | 0.04 | 3882 | 801 | 199 |
| 3G | 99.36 | 0.54 | 0.10 | 0.00 | 1334 | 543 | 0 |
| 3J | 99.35 | 0.53 | 0.11 | 0.00 | 1297 | 643 | 0 |
| 3K | 99.23 | 0.73 | 0.04 | 0.00 | 1792 | 198 | 0 |
| 3L | 98.99 | 0.95 | 0.06 | 0.00 | 2289 | 324 | 0 |
| 3W | 99.18 | 0.81 | 0.00 | 0.00 | 2091 | 0 | 0 |

Notes: DL = detection limit. Mg = 340 ppm; Fe = 445 ppm; Mn = 310 ppm.

present. Thus, ¹⁸O-depleted fluids, if once present, would be most plausibly interpreted as the result of authigenic mineral precipitation, as suggested by Lawrence and Gieskes (1981), especially in view of the Sr isotopic values that are consistent with Cretaceous seawater.

Values of δ^{18} OH₂O in the positive range can be produced by evaporative concentration of ¹⁸O in surface fluids (Lloyd, 1966), an alternative reasonably excluded in this tectonic setting. "Rock-dominated" fluid/rock interaction, in which the fluids acquire an isotopic signature that is shifted toward that of the rock by mineral dissolution or replacement, is a more likely mechanism for producing ¹⁸O-enriched fluids for calcite precipitation in this setting. Possible excursion of δ^{18} OH₂O into the positive range is a reasonable consideration in view of the Fe and Mn concentrations in the calcites reported here



Figure 3. Mn vs. Mg variation in early vacuolized calcite in Samples 149-899B-16R-2, 69-72 cm, and 149-897D-16R-4, 114-116 cm.

and the extreme degree of fluid/rock interaction evidenced by secondary porosity, Mg loss from the whole rock, and clay mineral precipitation (Milliken et al., this volume). However, at least three lines of evidence suggest that significantly positive values of $\delta^{18}OH_{20}$ can also be ruled out. First, although temperatures consistent with ¹⁸O-enriched fluids (up to 53°C for a $\delta^{18}OH_2O$ in the range of +7) are possible in this rift setting, the uniformity of 818Ocalcite argues against this sort of "hydrothermal" system because both temperature and δ^{18} OH₂O would have to have been maintained within narrow limits (or have covaried precisely) for the duration of precipitation of the multiple fracture-filling calcite generations. Second, two-phase fluid inclusions have not been observed among the abundant inclusions in the vein-filling calcite, which suggests a very low temperature of precipitation that is incompatible with ¹⁸O-enriched fluids over the observed range of $\delta^{18}O_{\text{calcite.}}$ Finally, the absence of Mg-bearing carbonate phases (dolomite or magnesite) and ⁸⁷Sr/⁸⁶Sr values that range narrowly about the values of Early to middle Cretaceous seawater (e.g., Burke et al., 1982; Koepnick et al., 1985; Ingram et al., 1994; Jones et al., 1994) suggest that dissolution of the serpentinite did not strongly overprint the composition of the fluid that mineralized the fractures.

Causes of Petrographic vs. Compositional Variation

The lack of systematic compositional trends (for both trace elements and isotopic values) across petrographic variations in calcite morphology and sequence of precipitation is an unexpected observation. Apparently, variation in calcite composition was not influenced by the same factors that affected calcite morphology. Rather, it seems likely that morphological variation in the crack-filling calcite was controlled by some factor—precipitation rate, for example—that is not strongly manifested in calcite composition. In addition, the lack of correlation between the composition and temporal sequences of calcite precipitation observed suggests that neither temperature nor fluid composition evolved in any systematic or significant way during vein filling. ⁸⁷Sr/⁸⁶Sr values that span nearly the total observed range for both vacuolized and clear calcites suggest that the sequence from "early" vacuolized calcite to "late" clear spar developed repeatedly during vein filling.

CONCLUSIONS

Relatively uniform δ^{13} C, δ^{18} O, and 87 Sr/ 86 Sr in the fracture-filling calcites at Sites 897 and 899 are most plausibly interpreted as the result of precipitation in cracks that were open to circulation of little-modified seawater at ambient ocean-bottom conditions (Neptunian

Table 3. Electron microprobe analyses of fracture-filling aragonite, Sample 149-897D-16R-4, 0-5 cm.

| Analysis | CaCO ₃ (mole%) | MgCO ₃ (mole%) | FeCO ₃ (mole%) | MnCO ₃ (mole%) | SrCO ₃ (mole%) | Mg (ppm) | Fe (ppm) | Mn (ppm) | Sr (ppm) |
|----------|------------------------------|------------------------------|------------------------------|------------------------------|------------------------------|-------------|-------------|-------------|-------------|
| 1 | 99.02 | 0.05 | 0.02 | 0.00 | 0.91 | 125 | 104 | 0 | 7790 |
| 2 | 97.83 | 0.00 | 0.02 | 0.04 | 2.11 | 0 | 89 | 204 | 18190 |
| 3 | 99.28 | 0.00 | 0.00 | 0.00 | 0.71 | 0 | 0 | 0 | 6140 |
| 4 | 97.73 | 0.04 | 0.00 | 0.02 | 2.22 | 90 | 0 | 130 | 18750 |
| 6 | 98.00 | 0.05 | 0.02 | 0.04 | 1.89 | 106 | 113 | 212 | 16070 |
| 8 | 98.12 | 0.03 | 0.00 | 0.00 | 1.84 | 78 | 0 | 0 | 15590 |
| 10 | 97.83 | 0.05 | 0.00 | 0.00 | 2.12 | 106 | 0 | 0 | 17940 |
| 15 | 98.36 | 0.05 | 0.00 | 0.03 | 1.56 | 115 | 0 | 151 | 13350 |

Notes: DL = detection limit. Mg = 340 ppm; Fe = 445 ppm; Sr = 185 ppm.

 Table 4. Stable isotopic results for vein calcite, Sites 897 and 899.

| Core, section, interval (cm) | $\delta^{13}C$ | δ ¹⁸ O | Sr ⁸⁷ /Sr ⁸⁶ | Standard deviation | Calcite type |
|---------------------------------|----------------|-------------------|------------------------------------|--------------------|-------------------|
| 149-897C- | | | | | |
| 64R-4, 16-19 | 1.5 | -0.4 | 0.70744 | 0.00002 | Sediment infill |
| 64R-4, 16–19 | 1.1 | -0.3 | | | Vacuolized |
| 64R-4, 16-19 | 1.4 | 0.5 | 0.70742 | 0.00005 | Clear |
| 64R-4, 16-19 | -0.6 | -0.7 | | | Clear |
| 64R-4, 16-19 | 1.4 | -0.7 | | | Sediment infill |
| 65R-1, 19-23 | -0.3 | 0.1 | | | Clear |
| 149-897D- | | | | | |
| 12R-1, 63-65 | 0.3 | 0.2 | | | Clear |
| 13R-5, 57-61 | -1.3 | -0.2 | 0.70741 | 0.00010 | Vacuolized |
| 13R-5, 57-61 | | | 0.70747 | 0.00003 | Clear |
| 16R-4, 0-5 | -0.8 | -0.1 | 0.70742 | 0.00010 | Clear (aragonite) |
| 16R-1, 114-116 | | | 0.70743 | 0.00003 | Vacuolized |
| 17R-6, 62-65 | | | 0.70739 | 0.00002 | Sediment infill |
| Site average | 0.29 | -0.18 | | | |
| 149-899B- | | | | | |
| 16R-4, 102-105 | 2.0 | 0.5 | | | Vacuolized |
| 18R-2, 135-139 | 2.1 | 0.8 | 0.70737 | 0.00006 | Vacuolized |
| 18R-2, 135-139 | 1.6 | 0.5 | | | Vacuolized |
| 18R-2, 135-139 | 0.7 | 0.8 | 0.70735 | 0.00006 | Clear |
| 16R-2, 69-72 | 1.9 | 0.4 | | | Vacuolized |
| 16R-2, 69-72 | 0.2 | 1.0 | | | Clear |
| 20R-1, 21-24 | 1.1 | -0.7 | | | Vacuolized |
| 20R-1, 21-24 | 0.7 | -0.2 | 0.70752 | 0.00003 | Vacuolized |
| 20R-1, 21-24 | 1.5 | 0.0 | 0.70750 | 0.00004 | Clear |
| Site average | 1.32 | 0.35 | 0.70743 | | |



Figure 4. Variation of δ^{18} O and δ^{13} C in fracture-filling calcites at Sites 897 and 899. Isotopic compositions from vein-filling calcite in serpentinites sampled during Leg 103 (Evans and Baltuck, 1988, table 2) are plotted for comparison.

fractures) in the Early to middle Cretaceous. This lends strong support to the notion that alteration (and especially calcitization) in the upper portions of the (acoustic) basement rocks at both sites (Shipboard Scientific Party, 1994a, 1994b; Gibson et al., this volume) relates to a period of submarine exposure of these ultramafic rocks in the period between initial rifting and the onset of significant sedimen-



Figure 5. Comparison of Sr isotopic values in fracture-filling calcites to Sr isotopic variations in Cretaceous seawater. ⁸⁷Sr/⁸⁶Sr values observed in vein-filling calcites at Sites 897 and 899 (here corrected by -0.0001 from measured values) fall within the shaded area. The line showing the approximate ⁸⁷Sr/⁸⁶Sr variation in seawater is generalized from the curve of Jones et al. (1994, figs. 3, 4). The timing of mass-flow deposition is constrained by bio-stratigraphic data (Shipboard Scientific Party, 1994a, 1994b). See text for discussion.



Figure 6. Field of possible temperature and $\delta^{18}O_{water}$ consistent with observed $\delta^{18}O_{calcite,}$ based on equation for calcite-H₂O oxygen isotopic equilibrium in Friedman and O'Neil (1977, figure 13). The vertical bar indicates the range of temperature possible for precipitation from a fluid of 0‰ (SMOW). See text for discussion.

tation. Variations in Fe and Mn in the calcites are likely the result of small and possibly very local fluctuations in the oxidation state of the precipitating fluids. The low concentrations of Mg and Sr, as compared to typical authigenic calcites in shallow-marine settings, are best interpreted as indicative of a low temperature of precipitation (cf., Morse and Mackenzie, 1990).

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